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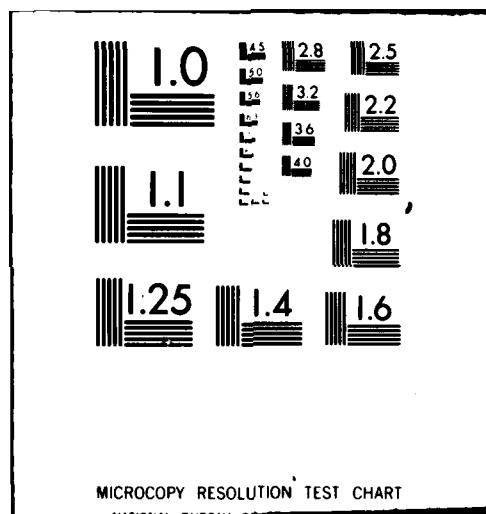


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Theoretical Studies of Metal Oxides

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FINAL REPORT

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Final Report

AFOSR-78-3677

Theoretical Studies of Metal Oxides

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Abstract. Detailed calculations are carried out of the potential energy curves of the low-lying singlet and triplet states of MgO and the electric dipole transition moments between the states are obtained. Using the results, a comprehensive analysis of spectral line data is possible and the mechanisms by which MgO is dissociated by photons can be identified. Preliminary estimates suggest a radiative lifetime of 2.1×10^{-8} s for the $B^1\Sigma^+$ state and of 2.8×10^{-4} s for the $A^1\Pi$ state. Some calculations on MgO^+ have been carried out. We predict an ionization potential for MgO of 7.9 eV.

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1. Introduction

We have been engaged in an attempt to employ sophisticated procedures to calculate to useful accuracy the potential energy curves and the transition dipole moments of the low-lying electronic states of the diatomic species MgO and MgO^+ . These data are essential to a successful analysis of spectral line observations (cf. Ikeda et al. 1977) in photoluminescence and to the application of saturation spectroscopy to the measurement of MgO in flames (cf. Pasternak, Baronavski and McDonald 1978). They are of interest also in the design of possible gas lasers and have direct application to atmospheric chemistry and to solar and stellar atmospheres.

Difficulties arising from the existence of metastable magnesium and oxygen dissociation products and from interactions with ionic states are formidable and their resolution was a substantial and arduous long term effort. It appears that the modifications and extensions which we and others (cf. Bauschlicher, Silver and Yarkony 1980, Bauschlicher et al. 1981) have put into effect have led to the development of methods which can be used to achieve reliable results. The methods have of course a more general utility.

Unfortunately support of the work by the Air Force Office of Scientific Research was terminated just at the point where sufficient numerical experiments had been completed which established the validity of the procedures and the program was entering its production phase. The results summarized in this

report, though of some immediate use, are still preliminary and there is little point in attempting a detailed discussion of their significance until they are available in final form. It is our intention, by one means or another, to complete the studies of MgO and MgO^+ , so that some reasonable return is gained from the very considerable cost in our time and efforts. Indeed, since the expiry of the grant, we have succeeded in obtaining some further results and they are included here.

2. Calculations on MgO

The calculation of the low-lying states of MgO used a total of 28σ and 16π Slater basis functions, of which 15σ and 8π were centered on Mg and 13σ and 8π were centered on O. With some modification, the atomic basis sets were obtained from the tables of atomic wavefunctions of Clementi and Roetti. The Mg basis used was the ground state $\text{Mg}(3s^2, ^1S)$ set supplemented with two $3p^-$, two $3d^-$ and one $4f$ -function. The exponents of the two $3p$ functions were optimized to minimize the energy of $\text{Mg}(3s3p, ^3P)$. The oxygen atomic basis used corresponded to the negative ion $\text{O}^-(2p^5, ^2P)$ set supplemented with two $3d^-$ and one $4f$ -polarization function.

A Hartree-Fock SCF calculation for the closed shell $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi^4 2\pi^4, ^1\Sigma^+$ configuration of MgO yielded an energy of -274.387934 hartree at the experimental internuclear separation $R = 3.3052$ au. This value was lower than previously

published SCF results, and was also lower than a SCF calculation of similar quality using a neutral oxygen atom basis.

We have previously reported results of valence configuration interaction (VCI) and limited first-order CI (LFOCI) calculations of the low-lying singlet and triplet states of MgO. It was demonstrated that computations of this size were inadequate to describe many quantitative features of the MgO system. We report here the extension of these calculations to the full valence MCSCF and first-order CI (FOCI) levels.

a) MCSCF calculations of the low-lying states of MgO

The low-lying states of $1,3\Sigma^+$, $1,3\Sigma^-$, $1,3\Pi$ and $1,3\Delta$ symmetries arise from the three lowest lying separated-atom limits: $\text{Mg}(^1\text{S}) + \text{O}(^3\text{P})$, $\text{Mg}(^1\text{S}) + \text{O}(^1\text{D})$ and $\text{Mg}(3\text{s}3\text{p}, ^3\text{P}) + \text{O}(^3\text{P})$. The ground $X^1\Sigma^+$ state of MgO dissociates adiabatically to the excited-atom limit $\text{Mg}(^1\text{S}) + \text{O}(^1\text{D})$. The consideration of these limits necessitated use of five valence orbitals in the calculations: 6σ , 7σ , 8σ , 2π and 3π . In the MCSCF, 6 electrons were distributed among the valence orbitals in all possible ways which couple to the correct symmetry. The core orbitals (1σ - 5σ , 1π) were fully occupied in all configurations. The remaining orbitals (9σ - 28σ , 4π - 16π , and 1δ - 6δ) formed the virtual space.

MCSCF calculations were performed on each of six states, and the results at internuclear separations between 3.0 a.u.

and 4.0 a.u. are given in Table 1. At the full-valence MCSCF level, the $^3\Pi$ state lies below the $^1\Sigma^+$ state (this is also true at the Hartree-Fock level).

b) FOCI calculations

The orbitals resulting from the MCSCF calculations were used to obtain first-order CI wavefunctions for the three lowest states of each symmetry. The FOCI wavefunction included the valence configurations together with additional configurations which were the result of a single excitation from the valence space into the virtual space. Table 2 gives the results between 3.0 au and 4.0 au for the lowest lying states.

The minimum energy value of -274.558276 au of the $X^1\Sigma^+$ state occurs at $R=3.36$ au. At $R = 20.0$ au, the energy of the separated atom $Mg(^1S) + O(^1D)$ limit is calculated to be -274.396374 au. This leads to a value of 4.41 eV for the adiabatic dissociation energy of the ground state of MgO.

The lowest singlet transitions are $X^1\Sigma^+ - A^1\Pi$ and $X^1\Sigma^+ - B^1\Sigma^+$. The difference in energy between the minimum of the $X^1\Sigma^+$ curve and the minimum of the $B^1\Sigma^+$ curve is about 20500 cm^{-1} , compared to an experimental value of $T_e = 19984\text{ cm}^{-1}$. The FOCI wavefunctions for both states used MCSCF orbitals determined for the $X^1\Sigma^+$ state. Values of the computed $X^1\Sigma^+ - B^1\Sigma^+$ transition dipole moments are given in Table 3. Calculation of transition moments between states whose CI wavefunctions involve different

molecular orbitals can be very expensive. For this reason we adopted the following approach in obtaining moments for the $X^1\Sigma^+-A^1\Pi$ transition (and other transitions in the triplet manifold). Transition moments were obtained at five points in the vicinity of the minima in the potential curves using in the CI molecular orbitals determined for each state. The calculations were repeated with (in this case) CI wavefunctions for the $A^1\Pi$ state which used $X^1\Sigma^+$ orbitals. Both sets of moments are included in Table 3. Vibrationally averaged matrix elements of the dipole between the $X^1\Sigma^+$ and $A^1\Pi$ states were obtained using each set of moments. The vibrationally averaged values differed by only about 5%, and on this basis it was decided that a FOCI wavefunction using $X^1\Sigma^+$ orbitals was an adequate description of the $A^1\Pi$ state for the purpose of obtaining transition moments. A complete transition moment curve was generated, and the vibrationally averaged matrix elements appear in Table 4.

Table 3 also contains transition moments for the $^3\Pi-^3\Sigma^+$ and $^3\Pi-^3\Sigma^-$ transitions. Vibrational averaging of full transition moment curves has not yet been completed for the triplet transitions.

Transition moments have been calculated by Huron, Malrieu and Rancurel (1974) between several states of MgO but only at one internuclear distance. Our values are significantly different though they do confirm that the $X^1\Sigma^+-B^1\Sigma^+$ transition

dipole moment is much larger than the $X^1\Sigma^+-A^1\Pi$ transition moment. Our preliminary estimate of the lifetime of the $A^1\Pi$ state is 2.8×10^{-4} s and of the $B^1\Sigma^+$ state is 2.1×10^{-8} s. Main et al. (1967) (see also Main and Schadee 1969), have derived an empirical oscillator strength of 1.7×10^{-3} for the absorption from the $X^1\Sigma^+$ to the $B^1\Sigma^+$ state, whereas we predict a value of 0.14, about two orders of magnitude larger.

c) The $X^2\Pi$ state of MgO^+

A MCSCF-FOCI study of the low-lying doublet states ($^2\Pi$, $^2\Sigma^+$, $^2\Sigma^-$) of MgO^+ has been started. The basis set was obtained from Clementi and Roetti's tables for $Mg^+(3s, ^2S)$ and $O(2p^4, ^3P)$. Polarization functions were added giving a total of 27 σ , 15 π and 6 δ basis functions. The valence space was defined to contain the 6 σ , 7 σ , 8 σ , 2 π and 3 π orbitals. A full-valence MCSCF potential curve was generated for the $X^2\Pi$ state of MgO^+ . The resulting molecular orbitals were then used to obtain a first-order CI (4260 configuration) potential curve, a portion of which appears in Table 5.

Although MgO^+ has not yet been observed, its ground state is predicted to be bound. The $X^2\Pi$ state of MgO^+ dissociates to $Mg^+(3s, ^2S) + O(2p^4, ^3P)$, which lies 5.679 eV above the $Mg(3s^2, ^1S) + O(2p^4, ^1D)$ adiabatic dissociation limit of MgO. If the MgO $X^1\Sigma^+$ curve and MgO^+ $X^2\Pi$ curve are shifted to match the

experimental asymptotic separation, one obtains for the ionization potential of MgO a value of 7.9 eV.

Table 1. MCSCF energies^a of low-lying MgO states

<u>symmetry</u>	<u>number of configurations</u>	<u>3.0</u>	<u>3.25</u>	<u>3.5</u>	<u>3.75</u>	<u>4.0</u>
3Π	126	-274.505604	-274.536455	-274.546173	-274.544419	-274.536602
$1\Sigma^+$	76	-274.525131	-274.542158	-274.542221	-274.533790	-274.521398
1Π	96	-274.501644	-274.532530	-274.542231	-274.540363	-274.532339
$3\Sigma^+$	70	-274.497639	-274.516017	-274.518167	-274.512043	-274.501944
$3\Sigma^-$	78	-274.319307	-274.370246	-274.399684	-274.417290	-274.428365
3Δ	67	-274.339973	-274.368487	-274.376485	-274.373784	-274.366326

^aIn atomic units

Table 2. FOCI energies^a

<u>symmetry</u>	<u>number of configurations</u>	<u>3.0</u>	<u>3.25</u>	<u>3.5</u>	<u>3.75</u>	<u>4.0</u>
$1^1\Sigma^+$	3090	-274.539918	-274.556965	-274.556502	-274.547270	-274.534049
3Π	7757	-274.516926	-274.547661	-274.557250	-274.555435	-274.547668
$1^1\Pi$	5247	-274.514946	-274.543346	-274.552901	-274.550867	-274.542682
$3\Sigma^+$	4358	-274.504449	-274.523005	-274.525273	-274.519227	-274.509179
$2^1\Sigma^+$	3090	-274.446134	-274.462145	-274.459971	-274.448599	-274.433114
$3\Sigma^-$	4486	-274.338700	-274.388825	-274.417701	-274.434861	-274.445547
3Δ	5161	-274.391492	-274.420567	-274.428748	-274.425624	-274.416225

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^aIn atomic units

Table 3. Transition moments in atomic units^(a)

transition	<u>3.0</u>	<u>3.25</u>	<u>3.5</u>	<u>3.75</u>	<u>4.0</u>
$X^1\Sigma^+ - B^1\Sigma^+$	1.597	1.483	1.340	1.172	.983
$X^1\Sigma^+ - A^1\Pi$.556	.614	.557	.489	.418
$X^1\Sigma^+ - A^1\Pi$ (b)	.624	.587	.529	.461	.390
$3\Pi - 3\Sigma^+$.212	.194	.171	.142	.109
$3\Pi - 3\Sigma^-$.491	.472	.455	.440	.422

(a) The dipole operator is either $\sum_j z_j$ or $\sum_j (x_j + iy_j)$

(b) Computed using $X^1\Sigma^+$ orbitals for both states.

Table 4. Vibration matrix elements (in au) of dipole moment between the $A^1\Pi$ v' , $J'=1$ and the $X^1\Sigma^+$ v'' , $J=0$ state

<u>v'/v''</u>	<u>0</u>	<u>1</u>	<u>2</u>
0	0.307	0.326	0.218
1	-0.319	-0.035	0.227
2	0.254	-0.174	-0.183

Table 5. Potential energy curve for the X^2_{II} state of MgO^+

<u>R(au)</u>	<u>E(au)</u>
2.5	-274.071643
3.0	-274.268698
3.25	-274.293514
3.5	-274.297273
3.75	-274.282328
4.0	-274.271436
4.5	-274.249636
5.0	-274.234518
6.0	-274.223147
20.0	-274.220511

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